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Quantitative Analysis (Gravimetric)

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Q U A N T I T A T I V E A N A L Y S I S.

(G R A V I M E T R I C)

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Author's Note:-

This work is the epitome of a course in Quantitative Analysis under the very careful supervision of Dr. Matthew Beardwood whose untiring interest and sound advise has made the study a real source of knowledge and pleasure. In general the course consisted of two half hour periods a week of recitation and discussion in conjunction with four hours of laboratory work.

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Introduction.

Chemical Analysis comprises two branches, namely, qualitative analysis and quantitative analysis, the object of the former being to ascertain the nature, that of the latter to determine the amount of the several component parts of any compound.

In quantitative analysis the object is attained according to circumstances, often by very different ways; the two methods most widely differing from each other are analysis by weight, or gravimetric analysis, and analysis by measure, or volumetric analysis.

Therefore, by way of definition, gravimetric analysis is that division of quantitative analysis which has for its object the conversion of the known constituents of a substance into forms or combinations which will admit of the most exact determination of their weight, and of which, moreover, the composition is accurately known.

General Directions.

Nothing less than absolute integrity, extreme accuracy and scrupulous cleanliness can be demanded of any chemist who wishes to be successful in his analyses. The countless possibilities of error through loss of materials or introduction of foreign matter require careful manipulation at all times in order that a reliability of a working accuracy may be established.

Evaporation of Liquids.

One phase of the work which calls for skillful operation on the part of the analyst is the evaportaion of liquids. Too great care cannot be taken to avoid the loss of solutions during the processes of evaporation, either from too violent ebullition, from evaporation to dryness and spattering or from evolution of gas during the heating. Steam baths are generally used unless the circumstances warrant other methods. In all cases it is quite advisable to cover the dish with a watchglass to prevent contamination from dust.

Liquids containing suspended matter (precipitates) should always be cautiously heated to eliminate the possibility of breaking the apparatus as is frequently caused by the occasional violent "bumping" of the liquid.

The transfer of liquids from one beaker to another should always be aided by the use of a stirring rod held firmly against the side or lip of the vessel so that the liquid may run down the rod into the receiving beaker with a minimum amount of splashing. Under all conditions the transfer should be made into perfectly clean glassware to avoid contamination. Also each delivering vessel should be thoroughly washed to insure complete transfer of its contents.

Reagents.

The testing and use of reagents is also an important feature of the analyst's work. Calculation of amounts of reagents

needed for an operation should be made whenever possible in order that large excesses which are frequently detrimental may be avoided.

All reagents, even distilled water, should be carefully tested as a precautionary measure against inferior chemicals. The responsibility of the purity of the reagents therefore lies solely with the individual and consequently gives the individual a greater confidence in the accuracy of his work.

Careful labeling of reagent bottles is an indispensable aid in the economy of time and a distinctly visible system is to be recommended in all cases.

Precipitation.

Successful precipitation must involve conditions which insure the nearest approximation to insolubility of the precipitated material, and the precipitate must also be in the form favorable for filtration and washing. In all precipitation the reagent should be added slowly, with constant stirring , and should be hot when circumstances permit. This slow addition is less likely to occasion contamination of the precipitate by the inclosure of other substances which may be in solution, or or the reagent itself.

For the complete removal of the precipitate from the containing vessel it is often necessary to employ a "policeman" which consists of a glass stirring rod covered at one end with a piece of of tightly fitting rubber. The flexibility of the rubber permits

the removing of the minute particles of precipitate without scratching the beaker.

Filtration and the Testing of Filtrates and Washings.

"Washed" filters and distilled water are quite essential to accurate analyses. The "washed" filter is one which is treated with hydrochloric and hydrofluoric acids and yields a definitely known weight of ash upon incineration. The value of such prepared papers is readily recognizable and the filter ash becomes a universal figure, generally 0.0024 grams for a 9 centimeter filter

Funnels of sixty degree angle give the most efficient results in filtering when the paper is folded to exactly fit in the angle. To be most successful the filter should allow the water to pass down the short stem of the funnel in an even stream, otherwise it produces an unnecessary annoyance. Under certain circumstances where the filter pump is used to increase the speed of filtration it becomes necessary to support the apex of the filter with either a perforated cone of platinum or parchment. In some special cases a Gooch filter is required. This is essnetially a perforated platinum crucible containing a mat of asbestos fibers fitted snugly in a porcelain funnel with the aid of a rubber strip which makes it airtight. The funnel when attached to a strong suction pump becomes an indispensable piece of apparatus for rapid filtration.

The filtrate should be allowed to run down the side of the receiving beaker instead of dropping, which often causes loss of liquids. Careful examination of the filtrate is a precaution-

ary measure against a finely divided precipitate which sometimes comes through with the filtrate. Refiltering, or the addition of another filter paper is the remedy recommended.

The process of washing precipitates by decantation is indeed a time saving feature consisting of pouring over the precipitates while still in the original vessel considerable quantities of wash water and allowing them to settle. The supernatant, clear wash water is then decanted through the filter without disturbing the precipitate and a new portion of water is added and the process repeated until it is desired to transfer the entire contents of the vessel to the filter for the final washing.

Gelatinous precipitates should never be allowed to dry before complete removal or foreign matter has been effected. Otherwise they are likely to shrink and crack and the further addition of wash water would pass through these channels only.

Solutions in general should be filtered while hot as far as possible since the motion of the liquid through the pores of the filter is retarded by friction and this for water at 100° C. is less than one-sixth of the resistance at 0° C.

The testing of all filtrates and wash waters lies at the foundation of all accurate work. Every original filtrate must be tested to prove complete precipitation of the coumpound to be separated and the wash water must be tested for the presence of the filtrate still on the filter. Since conditions of filtration vary so widely it is absolutely useless to trust one's

judgment with regard to the washing of the precipitates, the washing should invariably be tested.

Ignition of Precipitates.

With proper precautions a large number of precipitates may be ignited without previous drying, but if such precipitates can be dried without loss of time to the analyst (as e.g. over night) it is well to submit them to this process. However, it should be remembered that a partially dried precipitate requires more skill in handling during ignition than a thoroughly moist one.

In drying a precipitate the filter should be folded over it completely and the entire mass placed well at the base of the crucible which should then be placed so far above the lamp that no violent escape of steam is possible. After the filter and contents have dried the crucible should be placed on its side without a cover and the heat gently increased until the filter chars, but never above that point until the volatile organic matter of the paper has been expelled by dry distillation. The flame during this preliminary heating should be placed near the mouth of the crucible, but in all subsequent heatings the flame should be directed well to the base of the crucible to allow ready access of oxygen and to avoid the entrance of unburned gas which would act as a reducing agent. When the filter has charred the heat should be intensified to reddness until ignition is complete as noticed by the presence of a finely divided ash. The blast lamp should not be used for heating unless specially indicated.

The use and care of the Balances.

Owing to its extreme delicacy the chemical balance requires most careful manipulation and extreme care inorder that it may render the ultimate accuracy for which it was designed.

The usefulness of the instrument depends upon two exceedingly important points; first, its accuracy and second, it sensibility or delicacy.

First:- The instrument's accuracy depends upon the following conditions;-

(a) The fulcrum, or the point on which the beam rests, must lie above the centre of gravity of the balance.

(b) The points of suspension of the scales must be on an exact level with the fulcrum.

(c) The beam must be sufficiently rigid to bear without bending the greatest weight that the construction of the balance admitsof.

(d) The arms of the balance must be of equal length.

Second:- The sensibility of the chemical balance is determined principally by the three following conditions:

(a) The friction of the edges upon their supports must be as slight as possible.

(b) The centre of gravity must be as near as possible to the fulcrum.

(c) The beam must be as light as possible.

When considering the carein theuse of the balances the necessity of a sense of individual responsibility is coupled with a few hard and fast rules to be universally observed:-

(a) The balance pans should be brushed off and the adjustment of the balance tested before use.

(b) The beams should never be set in motion by lowering it forcibly, nor by touching the pans, but rather by means of the rider, and the swing should only be arrested after the needle passes the zero on the scale, otherwise the knife edges become dull and the balance inefficient.

(c) In testing the weight of a body the weights should be applied in the order they occur in the box and not haphazardly. A check on your record, as noted by the missing weights in your box, is made by noting the sum of the weights taken from the pan after the weighing in complete.

(d) The balance case should always be closed during the final weighing, when the rider is used, to protect the pans from the influence of air currents.

(e) No chemical substance should ever be place directly on the balance pan. Every substance weighed should be dry and cold as warm substances occasion air currents which prevent accurate results.

(f) Prompt attention to any derangment or inefficiency of the balance is absolutely essential to the aversion of serious damage.

Therefore, with due respect to all other manipulation of analysis an understanding knowlege of the care and use of the balances is to be regarded as of prime importance to the analyst using gravimetric methods.

III. Typical Gravimetric Analysis.

(Note:- Although several additional anaylses were performed in the laboratory the following ones have been regarded as typical by the author)

Determination of Chlorine in Sodium Chloride.

Owing the the presence of impurities which are so frequently found in commercial sodium chloride it was necessary to prepare the pure salt by the following procedure;-

About fifty grams of a sample of table salt were weighed out roughly on the balances, transfered to a beaker and covered with approximately 120 cc. of distilled water and stirred until the water was saturated and filtered. Concentrated hydrochloric acid (sp. gr. 1.20) was then added to the filtrate until the chloride just began to separate when gaseous hydrochloric acid was passed into the solution from a flask containing sodium chloride acted upon by sulphuric acid. This gas was washed before going into the solution by means of it passage through a concentrated aqueous solution of hydrochloric acid. A two inch inverted funnel served as a delivery tube in order to prevent the clogging of the salt at the termination of the tube. When the separation of the salt had apparently ceased it was removed by filtration upon a paper disk which was drained by suction. After the drainage had been completed the salt was washed with 25 cc. of hydrochloric acid (sp. gr. 1.12) in successive small portions, allowing the precipitate todrain completely after each addition. Finally the salt was washed with 5 cc. of water and this wash water tested for sulphates. The precipitate then being transfered to a porcelain

dish and heated until the decrepitation ceases and cooled in a desiccator after which it was placed in a weighing bottle and tightly stoppered until ready for analysis.

Analysis Procedure.

With the least possible amount of handling, the weighing bottle containing the sodium chloride was cleaned carefully and weighed accurately. About three grams of the contents of the bottle were cautiously dropped into a 300 cc. beaker and the exact weight determined by the difference of the weights of the weighing bottle. A second portion was similarly weighed into another beaker and the corresponding weights of the samples recorded in the notebook. Each portion was dissolved in 150 cc. of distilled water and about ten drops of nitric acid (sp. gr. 1.20) were added and then to this mixture was slowly added about 5 cc. in excess of the amount of silver nitrate needed to effect complete precipation with constant stirring. Heat was applied to boiling, with occasional stirring and continued until the precipitate settled promptly leaving a clear, supernatant liquid above. To the clear liquid was added a few drops of silver nitrate to make certain that the reagent was in excess and the liquid was then poured through a filter, allowing as much of the salt as possible to remain in the beaker. The filtrates, after being carefully tested, were replaced by clear beakers and the precipitates washed three or four times by decantation and finally washed upon the filter by means of a fine stream from the wash bottle until 3 cc. of the washings gave no cloudiness upon the addition of a drop of hydrochloric acid. The funnels, after careful drainage, were

covered with a moist filter paper and placed in an air over at a temperature of 100 to 110° C. until dried completely.

At the completion of the drying, the precipitate was carefully removed from the filter to a peice of glazed paper and covered with a watchglass to prevent loss and contamination. In the meantime the filter was rolled into a small cone and wound about the top with a small platinum wire and ignited over a clear and weighed crucible and the falled ash ignited until all the carbon had been expelled. The crucible was allowed to cool and two drops of nitric acid and one drop of hydrochloric acid were added to the ash and heated very cautiously to avoid spattering, until all the acids had been expelled. Then the main portion of the precipitate was carefully brushed into the cooled crucible and moistened with two drops of nitric and one of hydrochloric acid and again heated until the acids were expelled and the precipitate became white, when the temperature was gradually raised until the silver chloride fused. The crucible was cooled in the desiccator and weighed, after which was reheated and again weighed, after cooling until a constant weight varying not more than 0.0003 gram in two consecutive weighings.

The following data and calculation represent the analysis:-

Atomic weight of Cl — — — — = 35.46

" " of Na — — — = 23.00

Molecular weight of NaCl — — = 58.46

$\therefore$ Cl:NaCl = 35.46 : 58.46 = x : 1

$$58.46x = 35.46$$

$$x = .606 \text{ or } \underline{60}.6\ \%\ \text{Cl in NaCl}$$

Atomic weight of Cl = 35.46

" " of Ag = 107.88

Molecular weight of AgCl = 143.34

∴ Cl : AgCl = 35.46 : 107.88 = x : 1

$107.88x = 35.46$

$x = .247$ or 24.7 % Cl in AgCl.

Weight of weighing bottle and NaCl = 18.7469 grams

2nd. " " " " " " = 18.4387 "

" " NaCl used = 0.3082 "

Weight of crucible and AgCl = 9.566 Grams

" " " alone = 8.83 "

" " AgCl = 0.736 "

∴ Weight of Cl in NaCl used .3082 x .606 = .1867692 grams

" " Cl in AgCl obtained .736 x .247 = .181792 "

Amount of error as deficit = 0.0049772 "

or approximately 0.2 %

Analysis of Limestone.

Determination of Water.

To determine the amount of moisture in the sample, which was representative of the entire portion because of pieces from various portions of the rock being used, about 25 grams were transfered to a weighing bottle with a ground glass stopper and heated at a temperature of 105 C. for intervals of one hour. At the end of each interval the tube was cooled in a desiccator and weighed until two concordant weights in two consecutive weighings were recorded and then the calculation for water content was computed:-

Weight of weighing tube and limestone = 56.8755 grams
" " " " alone = 31.34 "
" " limestone used = 24.5355 "

Weight of limestone and tube before heating = 56.8755 grams
" " " " " after " = 56.85 "
" " moisture content = 0.0255 "

∴ Moisture in sample 2.55 ÷ 24.5355 = 0.103 %

Determination of the Insoluble Matter and Silica.

About 5 grams of the powdered sample of limestone was weighed out into a 250 cc. casserole and covered with a watchglass after adding 25 cc. of water and then 50 cc. of hydrochloric acid (sp. gr. 1.12) in small portions. The solution was warmed gently until no further signs of dissolving appeared and then evaporated to dryness on the water bath. Upon the addition of a mixture of 5 cc. of water and 5 cc. of hydrochloric acid it was again evapor-

ated to dryness and finally heated for at least one hour at a temperature of 120° C. Pouring over this residue about 50 cc. of dilute hydrochloric acid and boiling for five minutes it was then filtered and washed twice with hydrochloric acid and then with hot water until free from chlorides. After transfering the filter and contents to a platinum crucible it was dried and ignited to a constant weight. The residue represented the insoluble matter and silica from the soluble silicates. The percentage was calculated from the following data:

Weight of crucible and residue	=	8.8600	grams
" " " alone	=	8.8063	"
" " residue	=	0.0537	"
" " filter ash	=	0.0024	"
" " insoluble matter	=	0.0513	"

.: Insoluble matter in the 5 grams used is represented by

$$5.13 \div 5 = 1.026\ \%$$

Determination of Ferric Oxide and Alumina.

To the filtrate from previous determination was added 10 cc. of ammonium chloride solution and ammonium hydroxide until the solution smelled strongly of ammonia. Then, after the addition of 5 cc. of bromine water and boiling for five minutes more ammonium hydroxide was added. A warming of the solution until it barely smelled of ammonia made it ready for filtering after standing for a few moments. The filter was washed twice with hot water and then with 25 cc. of hot dilute hydrochloric acid and again with hot water five times. To the filtrate ammonium hydroxide and bromine water was again added and the precipitation was

repeated. The precipitate being the same as on the filter is collected on the filter already used, washed free of chloride, ignited and weighed. The residue, consisting of ferric oxide, alumina and manganic oxide rendered the following calculation:

Weight of crucible and residue = 9.0824 grams

" " crucible empty = 9.0718 "

" " residue = 0.0082 "

.; The ferric oxide and alumina in the sample -

0.82 ÷ 5.02 = 0.163 %

Determination of Calcium

To the combined filtrates from the previous determination was added 5 cc. of ammonium hydroxide and then it was transferred to a 500 cc. graduated flask and gradually diluted up to 500 cc. exactly. One fifth of the solution was measured off into a 400 cc. beaker after a thorough mixing. the measured solution was subsequently diluted to 250 cc. with distilled water, heated to boiling and ammonium oxalate solution was added in excess with vigorous stirring. After boiling for two minutes the precipitate was allowed to settle in the solution for a half an hour and then decanted through a filter. The filtrate was tested by the addition of a few cc. of the precipitant to insure complete precipitation and allowing the mixture to stand for fifteen minutes and after a non-appearance of a precipitate of the former precipitate on the filter was redissolved with warm dilute hydrochloric acid by running it through the filter. The filter in turn was washed five times with water and finally with ammonia and the solution diluted to 250 cc. and brought to a boil at which point 1 cc. of

ammonium oxalate was added, then ammonia in slight excess. After boiling for two minutes the solution was set aside for half an hour and filtered through the first filter and washed free of chlorides. The precipitate was then ready for ignition, which was done without previous drying and after the filter had burned the filtrate was heated for three-fourths of an hour in the hottest bunsen flame and finally three minutes at the blast lamp. Repeated the operation until a constant weight was obtained and from the residue, calcium oxide, the percentage in one-fifth of the sample was calculated with the aid of the following data:

Weight of crucible and residue = 9.624 grams

" " " empty = 9.0818 "

" " residue of CaO = 0.5422 "

Ca : CaO = 40 : 56 = x : 0.5422

56x = 21.6880

x = 0.3872 grams

∴ The calcium in sample 38.72 + 1.01 = 38.33 %

Should be 40 % in pure $CaCO_3$

Determination of Carbon Dioxide.

About five grams of the original sample of limestone was weighed out accurately and covered with about 100 cc. of distilled water in a 500 cc. flask fitted with a dropping funnel and a delivery tube. Sulphuric acid (concentrated) was poured into the dropping funnel and to the delivery tube were attached two more 500 cc. flasks in a series containing a strong solution of barium chloride which for the purpose of absorbing the evolved carbon dioxide gas. Of course, in order to accomplish this the

inlets of the wash bottles were below the surfaces of the barium chloride solutions. Everything being in readiness and especially airtight the sulphuric acid was permitted to drop very slowly into the mixture of water and powdered limestone, taking special care that no surplus gas escaped from the last bottle as a result of too rapid evolution. After all the effervescent action of the acid ceased giving evidence of the complete evolution of the carbon dioxide of the sample water was allowed to run into the gererating flask fillingbit to its capacity. Then each of the wash bottles was agitated vigorously to aid solution of the carbon dioxide and after about fifteen minutes the wash bottles were opened and boiling hot water introduced bringing down a heavy precipitate of barium carbonate ($BaCO_3$), with the aid of a little ammonium hydroxide. The contents of the two bottles were filtered on a large filter and after drainage the precipitate was dissolved from the filter paper by pouring through it strong hydrochloric acid. To this solution was added strong sulphuric acid until the precipitation of barium sulphate was complete. After considerable stirring the mixture was filtered and the precipitate washed free of chlorides, dried and ignited in a crucible to a constant weight. Resulting weight of the barium sulphate gave rise to the percentage of carbon dioxide present in the sample of limestone as noted by the following data:

Weight of crucible and barium sulphate = 20.4126 grams

" of " empty = 9.0786 "

" " barium sulphate obtained = 11.334 "

$BaSO_4 : BaCO_3 = 233 : 197 = 11.334 : x$

$233\,x = 2231.798$

$x = 9.58$ wt. $BaCO_3$

$BaCO_3 : CO_2 = 197 : 44 = 9.58 : x$

$197x = 421.52$

$x = 2.14$ grams wt. of CO_2

.: Percentage of CO_2 $214 - 5 = 42.8\ \%$

From pure $CaCO_3$ the percentage for CO_2 is 44.

Determination of the Total Iron in Haematite.

The ore was ground into a very fine powder by the use of a steel mortar and pestle and about 1.5 grams of the sample was introduced into a long-necked 500 cc. flask with some strong hydrochloric acid and heated until all the ore dissolved, the flask, however, being in an inclined position so as to prevent the loss of material by heavy spattering of the viscid liquid. Then small portions of potassium chlorate were added until the solution smelled strongly of chlorine whereupon the heating was continued until the least trace of chlorine was no longer perceptible. The solution was diluted to about 250 cc. with distilled water and stoppered with a closely fitting rubber stopper, containing a piece of glass tubing about ten inches long and open at both ends. The boiling was continued in the oblique for about fifteen minutes to insure the complete expulsion of the chlorine gas. While the solution was continuously boiling the cork was removed and a piece of clean, pure copper foil fastened to a platinum wire was lowered slowly into the solution after it had become warm by suspending it above the solution for a few minutes, thus preventing the liquid from spiriting. When finally immersed the copper foil was so arranged as to be always entirely below the surface of the liquid and the flask tightly stoppered, with the

continuous boiling going on all through the various operations without interruption. The boiling was kept from being too violent at all times and continued until the solution became colorless, showing the completion of the reduction which required about one and three quarter hours.

After the completion of the reduction the cork was removed and the strip withdrawn, while the solution was still boiling, and I lowered it into a beaker of distilled water and then rinsed with fresh distilled water and finally dried between pieces of blotting paper and weighed immediately. The loss of weight represented the amount of copper used in the reduction according to the equation $Fe_2Cl_6 \quad 2Cu \quad 2FeCl_2 \quad Cu_2Cl_2$.

Hence for every gram of copper dissolved there was a relative portion of iron present as noted by the following determination:

Weight of copper strip before immersion = 6.505 grams

" " " " after " = 5.416 "

" " copper dissolved = 1.089 "

Copper : Iron = 63 :. 56 = 1.089 : x

$63x = 60.984$

$x = 0.968$ grams = wt. of Fe

.: Percentage of iron in the 1.5 grams 96.8 - 1.5 64.53 %

In pure Fe_2O_3 -- $Fe_2O_3 : Fe_2 = 160 : 112 = 1. : 0.7$ or 70%

Hence 64.53 - 0.7 = 92.2 % pure Fe_2O_3 in the Haematite.

Conclusion

As will be seen from the preceding determinations quantitative analysis and especially gravimetric analysis enables one to determine the exact composition of the earth's various constituents as well as the products of industry. Similar analyses form the very foundation of countless industries of the world which depend on chemical analysis for their success or failure and as a result of its prime importance to industry various schemes of charts and tables have been carefully computed for convenience in analysis and consequently to-day most analytic work becomes routine and only the research chemist has the new method to discover and place in use. In general, chemical analysis is at the very basis of our everyday life in some form or other.

The End.